Zinc(II) and cadmium(II) coordination polymers containing phenylenediacetate and bis(imidazol-1-ylmethyl)benzene linkers: the effect of ligand isomers on the solid state structures

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Abstract

This work presents a systematic investigation of the reactions of *o*-, *m*- and *p*-phenylenediacetic acid with Zn(II)/Cd(II) salts in the presence of different semi-rigid *o*-, *m*- and *p*-bis(imidazol-1-ylmethyl)benzene co-ligands. Fourteen new coordination polymers – $\{[Zn(\mu\text{-opda})(\mu\text{-mbix})]\cdot 0.5H_2O\}_n$ (**1**), $\{[Zn(\mu\text{-mpda})(\mu\text{-obix})]\cdot H_2O\}_n$ (**2**), $\{[Zn_2(\mu\text{-mpda})_2(\mu\text{-mbix})_2]\cdot 5H_2O\}_n$ (**3**), $\{[Zn(\mu\text{-mpda})(\mu\text{-mbix})]\cdot 2H_2O\}_n$ (**4**), $\{[Zn(\mu\text{-mpda})(\mu\text{-pbix})]\cdot 0.5H_2O\}_n$ (**5**), $[Zn(\mu\text{-ppda})(\mu\text{-obix})]_n$ (**6**), $\{[Zn(\mu\text{-ppda})(\mu\text{-mbix})]\cdot 0.5H_2O\}_n$ (**7**), $\{[Zn(\mu\text{-ppda})(\mu\text{-pbix})]\cdot H_2O\cdot DMF\}_n$ (**8**), $\{[Cd(\mu\text{-mpda})(\mu\text{-obix})_{1.5}]\cdot H_2O\}_n$ (**9**), $\{[Cd(\mu\text{-mpda})(\mu\text{-obix})]\cdot H_2O\}_n$ (**10**), $\{[Cd(\mu\text{-mpda})(\mu\text{-mbix})(H_2O)]\cdot H_2O\}_n$ (**11**), $[Cd(\mu_3\text{-ppda})(\mu\text{-obix})]_n$ (**12**), $[Cd(\mu_3\text{-ppda})(\mu\text{-mbix})]_n$ (**13**) and $[Cd(\mu_3\text{-ppda})(\mu\text{-pbix})]_n$ (**14**) (o/m/ppda = 1,2/1,3-/1,4-phenylenediacetate, o/m/pbix = 1,2-/1,3-/1,4-bis(imidazol-1-ylmethyl)benzene) – have been prepared and structurally characterized. Two of the complexes were found to possess one-dimensional (1D) structures, eleven complexes were found to be two-dimensional (2D) coordination networks and one of the complexes was found to be a three-dimensional (3D) coordination network. Of the 1D structures, **3** forms nanotubes,

whereas in **8** pairs of pbix ligands bridge the zinc(II) centers to generate $Zn_2(pbix)_2$ dimers, which in turn are linked together by pairs of ppda linkers to give chains. Compound **5** contains a 4-fold interpenetrated 3D framework. The structure of **10** contains interpenetrated 2D frameworks, leading to a three-dimensional gross structure. The thermal stabilities and luminescent properties for **1**−**14** are also reported.

Keywords: Coordination polymer, Phenylenediacetic acid, Bis(imidazole) derivative, Hydrothermal Synthesis, Zinc(II) complex Cadmium(II) complex.

Introduction

The synthesis of coordination polymers (CPs) with different structural properties and functionalities is currently a very active research area[1, 2]. In recent years, a large number of coordination polymers have been synthesized to investigate the effect of organic linkers on their structural properties. CPs have been exploited for many different technologies[3-5] including gas storage[6], separation[7], catalysis[8] and bioapplications[9, 10].

The selection of anionic and neutral ligands is arguably the most important parameter in the design and synthesis of these materials[11, 12]. In the construction of CPs, aromatic and aliphatic polycarboxylate ligands, especially aromatic polycarboxylates have been extensively used and continued to be popular[13-16]. Recently, semi-rigid polycarboxylates which possess both aromatic and aliphatic groups have attracted considerable attention in CP chemistry[17-33]. These ligands are excellent candidates for the formation of CPs with interesting properties. Semi-rigidity affords the potential for changes in coordination ability following crystal-to-crystal transitions[34, 35], while maintaining the potential for porosity, which is often not possible with very flexible linkers due to their propensity to form more close-packed structures. A considerable amount of research has been carried out using a combination of anionic polycarboxylate and neutral *N*,*N*′-donor ligands, and mixed-ligand coordination polymers, assembled from polycarboxyate and nitrogen-rich co-ligands have been shown to form high-dimensional polymeric structures often with novel topologies. However, most of the previous work in this area has focused on utilizing rigid aromatic polycarboxylate ligands and *N*,*N*′-donor co-ligands with different metal ions[23-26].

This study aims to investigate the effect of using semi-rigid organic molecules as both the anionic and neutral linkers in mixed-ligand coordination polymers. Both phenylenediacetates and bis(imidazol-1-ylmethyl)benzenes contain rigid aromatic rings and more flexible methylene groups, and they can form cis and trans conformations via rotation around the C–C bonds. In addition, the choice of phenylenediacetates as the anionic linkers and

bis(imidazol-1-ylmethyl)benzenes as the neutral linkers, allows a systematic investigation of the relative orientations of the functional groups on the coordination polymer structure since both ligands are available as *o*-, *m*- and *p*-isomers. We have therefore systematically investigated the reactions of zinc(II) and cadmium(II) salts with *o*-, *m*- and *p*-phenylenediacetic acid (H_2opda, H_2mpda and H_2ppda) in the presence of *o*-, *m*- and *p*-bis(imidazol-1-ylmethyl)benzene (obix, mbix and pbix).

There are a number of previous studies using phenylenediacetates with *N*,*N*'-donor co-ligands[23, 25, 26, 28], but those employing semi-rigid bis(imidazole) derivatives as neutral ligands are extremely limited[22, 31, 36].

In this study the effect of temperature, pH, metal source, and solvent in the formation of coordination polymers were investigated. Fourteen new coordination polymers have been synthesized and the compounds have been characterized by elemental analysis, IR spectroscopy, and X-ray single crystal and X-ray powder diffraction analyses. The thermal and photoluminescence properties of the complexes were also investigated.

Experimental section

All chemicals were commercially available and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400C Elemental Analyzer. IR spectra were recorded on a Bruker Tensor 27 FT−IR spectrometer using KBr pellets in the range of 400−4000 cm^{-1}. Thermal analyses (TG, DTG and DTA) were carried out with a Perkin Elmer Diamond TG/DTA Thermal Analyzer in the static air atmosphere with a heating rate of 10 ºC/min in the temperature range of 30–700 °C. Powder X-ray diffraction patterns (PXRD) were recorded on a Rikagu Smartlab X-ray diffractometer operating at 40 kV and 30 mA with Cu-Kα radiation (λ = 1.5406 nm). The photoluminescence (excitation and emission) spectra for the solid complex samples were determined with a Perkin-Elmer LS-55 Fluorescence spectrometer.

Synthesis of {[Zn(μ-opda)(μ-mbix)]·0.5H_2O}$_n$ (1)

A mixture of H_2opda (0.7 mmol, 0.15 g), Zn(O_2CMe)$_2$·2H_2O (0.7 mmol, 0.17 g), mbix (0.8 mmol, 0.21 g) and DMF/H_2O (32 mL, v:v = 1:3) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 120 ºC for 7 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **1** were collected by filtration and washed with water. Anal. calcd. for $C_{96}H_{92}N_{16}O_{17}Zn_4$: C 57.55, H 4.63, N 11.19. Found: C 56.99, H 4.67, N 11.27. IR (KBr, cm^{-1}): 3426w, 3128w, 2912w, 1604vs, 1517m, 1446m, 1360vs, 1273m, 1211w, 1096w, 950w, 818m, 730s, 652m, 587m.

Synthesis of {[Zn(μ-mpda)(μ-obix)]·H_2O}$_n$ (2)

A mixture of H_2mpda (0.8 mmol, 0.15 g), Zn(O_2CMe)$_2$·2H_2O (0.7 mmol, 0.16 g), obix (0.8 mmol, 0.18 g) and H_2O (30 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 170 ºC for 3 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **2** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{24}N_4O_5Zn$: C 51.10, H 51.10, N 5.90. Found: C 50.70, H 4.09, N 5.16. IR (KBr, cm^{-1}): 3444w, 3109w, 2976w, 1584vs, 1531m, 1374vs, 1291w, 1096m, 949w, 837m, 713s.

Synthesis of {[Zn_2(μ-mpda)$_2$(μ-mbix)$_2$]·5H_2O}$_n$ (3)

A mixture of H_2mpda (0.5 mmol, 0.10 g), Zn(O_2CMe)$_2$·2H_2O (0.5 mmol, 0.11 g), mbix (1 mmol, 0.24 g), NaOH (0.5 mmol, 0.02 g) and H_2O (24 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 120 ºC for 5 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **3** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{24}N_4O_5Zn$: C 53.30, H 5.03, N 10.36. Found: C 52.85, H 5.26, N 10.36. IR (KBr, cm^{-1}): 3419w, 2950w, 1593vs, 1525m, 1444m, 1386vs, 1267m, 1232w, 1095w, 950w, 854m, 721s, 665m, 574m.

Synthesis of {[Zn(μ-mpda)(μ-mbix)]·2H_2O}$_n$ (4)

A mixture of H_2mpda (0.5 mmol, 0.10 g), Zn(O_2CMe)$_2$·2H_2O (0.5 mmol, 0.11 g), mbix (0.1 mmol, 0.24 g) and DMF/H_2O (24 mL, v:v = 1:3) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 120 ºC for 5 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **4** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{24}N_4O_5Zn$: C 51.10, H 51.10, N 5.90. Found: C 50.70, H 4.09, N 5.16. IR (KBr, cm^{-1}): 3403w, 2939w, 1614vs, 1505m, 1432m, 1354vs, 1262m, 1211w, 1029w, 939w, 837m, 720s, 669m, 546m.

Synthesis of {[Zn(μ-mpda)(μ-pbix)]·0.5H_2O}$_n$ (5)

Complex **5** was prepared in a similar manner to **4**, but using pbix (1 mmol, 0.24 g) instead of mbix. Anal. calcd. for $C_{48}H_{46}N_8O_9Zn_2$: C 57.10, H 4.59, N 11.10. Found: C 56.48, H 4.76, N 11.19. IR (KBr, cm^{-1}): 3448w, 3114m, 3026w, 2977w, 2922w, 1593vs, 1527m, 1373s, 1240w, 1105w, 948m, 854w, 758s.

Synthesis of [Zn(μ-ppda)(μ-obix)]$_n$ (6)

A mixture of H_2ppda (0.8 mmol, 0.15 g), Zn(O_2CMe)$_2$·2H_2O (0.7 mmol, 0.16 g), obix (0.8 mmol, 0.18 g) and H_2O (30 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 170 ºC for 3 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **6** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{22}N_4O_4Zn$: C 58.08, H 4.43, N 11.29. Found: C 58.14, H 4.38, N 11.20. IR (KBr, cm^{-1}): 3107w, 2902w, 1619m, 1590vs, 1375vs, 1249w, 1110m, 944w, 862m, 717s.

Synthesis of {[Zn(μ-ppda)(μ-mbix)]·0.5H_2O}$_n$ (7)

A mixture of H_2ppda (0.7 mmol, 0.15 g), Zn(O_2CMe)$_2$·2H_2O (0.7 mmol, 0.17 g), mbix (0.8 mmol, 0.21 g) and H_2O (30 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion

bomb and sealed then heated at 170 ºC for 5 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **7** were collected by filtration and washed with water. Anal. calcd. for $C_{48}H_{46}N_8O_9Zn_2$: C 52.10, H 4.59, N 11.10. Found: C 52.04, H 4.74, N 8.00. IR (KBr, cm^{-1}): 3471w, 3134w, 1608m, 1530vs, 1443m, 1361vs, 1273m, 1211w, 1107w, 953w, 860m, 705s, 652m, 574m.

Synthesis of {[Zn(μ-ppda)(μ-pbix)]·H_2O·DMF}$_n$ (8)

A mixture of H_2ppda (0.5 mmol, 0.10 g), $Zn(O_2CMe)_2·2H_2O$ (0.5 mmol, 0.11 g), pbix (0.25 mmol, 0.06 g) and DMF/H_2O (40 mL, v:v = 1:1) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 160 ºC for 5 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **8** were collected by filtration and washed with water. Anal. calcd. for $C_{27}H_{31}ZnN_5O_6$: C 55.25, H 5.32, N 11.93. Found: C 57.36, H 4.80, N 11.47. IR (KBr, cm^{-1}): 3461w, 3120w, 3015w, 2967w, 1615vs, 1530m, 1432m, 1372vs, 1290m, 1250w, 1106w, 948w, 869m, 722s, 658m, 530m.

Synthesis of {[Cd(μ-mpda)(μ-obix)$_{1.5}$]·H_2O}$_n$ (9) and {[Cd(μ-mpda)(μ-obix)]·H_2O}$_n$ (10)

A mixture of H_2mpda (0.7 mmol, 0.15 g), $Cd(O_2CMe)_2·2H_2O$ (0.7 mmol, 0.21 g), obix (0.7 mmol, 0.18 g) and H_2O (30 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 170 ºC for 3 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **9** were collected by filtration and washed with water. Anal. calcd. for $C_{31}H_{31}N_6O_5Cd$: C 54.75, H 4.60, N 12.36. Found: C 53.73, H 4.70, N 11.89. IR (KBr, cm^{-1}): 3392w, 3123w, 2928w, 1566vs, 1515m, 1445m, 1391vs, 1283m, 1236w, 1079w, 933w, 837m, 733s, 656m, 532m.

After standing for 1 week, colorless crystals of **10** were harvested from the reaction mixture and washed with water. Anal. calcd. for $C_{24}H_{24}N_4O_5Cd$: C 51.39, H 4.31, N 9.99. Found: C 50.73,

H 4.52, N 9.93. IR (KBr, cm^{-1}): 3500w, 3137w, 2904w, 1550vs, 1522m, 1432m, 1394vs, 1239m, 1084w, 940w, 850m, 746s, 654m, 532m.

Synthesis of $\{[Cd(\mu\text{-mpda})(\mu\text{-mbix})(H_2O)]\cdot H_2O\}_n$ (11)

A solution containing $Cd(O_2CMe)_2\cdot 2H_2O$ (0.7 mmol, 0.21 g), H_2mpda (0.7 mmol, 0.15 g) and mbix (0.7 mmol, 0.18 g) in water (30 mL) was poured into a 100 mL round-bottom flask. The resulting mixture was stirred for 30 min at room temperature and then was heated in a microwave oven for 30 min with the power set at 600 W. After irradiation, the flask was allowed to cool to room temperature. A small quantity of colorless crystals of **11** were collected by filtration and washed several times with water.

Synthesis of $[Cd(\mu_3\text{-ppda})(\mu\text{-obix})]_n$ (12)

A mixture of H_2ppda (1 mmol, 0.20 g), $Cd(O_2CMe)_2\cdot 2H_2O$ (1 mmol, 0.27 g), obix (1.2 mmol, 0.28 g) and DMF/H_2O (32 mL, v:v = 1:3) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 120 ºC for 7 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **12** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{22}N_4O_4Cd$: C 53.10, H 4.08, N 10.32. Found: C 52.76, H 3.78, N 10.77. IR (KBr, cm^{-1}): 3131w, 3108w, 2932vs, 2826m, 1592m, 1578vs, 1505m, 1358w, 1235m, 1080w, 937w, 855w, 716s.

Synthesis of $[Cd(\mu_3\text{-ppda})(\mu\text{-mbix})]_n$ (13)

A similar synthetic method to that of **12** was used except that mbix (1 mmol, 0.21 g) was used instead of obix. Anal. calcd. for $C_{24}H_{22}N_4O_4Cd$: C 50.10, H 4.08, N 10.38. Found: C 49.70, H 3.83, N 9.83. IR (KBr, cm^{-1}): 3115w, 2922w, 1566vs, 1512m, 1382vs, 1243w, 1103m, 937m, 855m, 723s.

Synthesis of $[Cd(\mu_3\text{-ppda})(\mu\text{-pbix})]_n$ (14)

A mixture of H_2ppda (0.8 mmol, 0.15 g), $CdCl_2$ (0.8 mmol, 0.14 g), pbix (0.8 mmol, 0.21g) and DMF (30 mL) was placed in a 45 mL Parr brand teflon-lined acid digestion bomb and sealed then heated at 140 ºC for 6 days, and then cooled at a rate of 5 ºC h^{-1} to room temperature. Colorless crystals of **14** were collected by filtration and washed with water. Anal. calcd. for $C_{24}H_{22}N_4O_4Cd$: C 53.10, H 4.08, N 10.32. Found: C 51.82, H 4.09, N 10.57. IR (KBr, cm^{-1}): 3123w, 3106w, 2925w, 1557vs, 1511m, 1382vs, 1234w, 1089m, 936m, 836m, 724s.

X-Ray diffraction analysis

Suitable crystals of **1**-**14** were selected for data collections which were performed on a Bruker APEX-II diffractometer equipped with a graphite-monochromatic Mo-K_α radiation at 296 K. The structures were solved by direct methods using SHELXS-97[37] and refined by full-matrix least-squares methods on F^2 using SHELXL-97[37] from within the WINGX [38] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from difference maps and then treated as riding atoms with C-H distances of 0.93-0.97 Å. All other H atoms were located in a difference map refined subject to a DFIX restraint. Molecular diagrams were created using MERCURY [39]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [40]. Details of data collection and crystal structure determinations are given in Tables 1 and 2. Connectivity within framework structures was analyzed using OLEX[41].

Supplementary Material

Further details of the structural analyses, together with X-ray powder diffraction patterns, photoluminescence spectra and thermogravimetric analyses are given in the ESI. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 1022032 for **1**, 1046226 for **2**, 1046227 for **3**, 1046228 for **4**, 1046229 for **5**, 1498065 for **6,** 1416919 for **7**, 1416917 for **8,** 1416918 for **9**, 1417524 for **10**, 1416920 for **11,** 1022036 for **12**, 1022037 for **13** and 1022038 for **14**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

3. Results and Discussion

Prior to commencing this study, systematic investigations using zinc(II) and cadmium(II) with bis(imidazole) derivatives and semi-rigid phenylenediacetates were rare[22, 36, 42]. It was therefore one of the aims of the research to investigate the synthesis conditions and methods required for the formation of coordination polymers as well as determining the effects of the conditions on the structures adopted.

Reactions were carried out with zinc(II) and cadmium(II) salts using *o*-, *m*- or *p*-phenylenediacetic acid (H_2opda, H_2mpda and H_2ppda) together with *o*-, *m*- or *p*-bis(imidazol-1-ylmethyl)benzene (obix, mbix and pbix) in a variety of solvents. From these reactions, the following compounds were isolated and structurally characterized: {[Zn(μ-opda)(μ-mbix)]·0.5H_2O}$_n$ (**1**), {[Zn(μ-mpda)(μ-obix)]·H_2O}$_n$ (**2**), {[Zn_2(μ-mpda)$_2$(μ-mbix)$_2$]·5H_2O}$_n$ (**3**), {[Zn(μ-mpda)(μ-mbix)]·2H_2O}$_n$ (**4**), {[Zn(μ-mpda)(μ-pbix)]·0.5H_2O}$_n$ (**5**), [Zn(μ-ppda)(μ-obix)]$_n$ (**6**), {[Zn(μ-ppda)(μ-mbix)]·0.5H_2O}$_n$ (**7**), {[Zn(μ-ppda)(μ-pbix)]·H_2O·DMF}$_n$ (**8**), {[Cd(μ-mpda)(μ-obix)1,5]·H_2O}$_n$ (**9**), {[Cd(μ-mpda)(μ-obix)]·H_2O}$_n$ (**10**), {[Cd(μ-mpda)(μ-mbix)(H_2O)]·H_2O}$_n$ (**11**), [Cd(μ_3-ppda)(μ-obix)]$_n$ (**12**), [Cd(μ_3-ppda)(μ-mbix)]$_n$ (**13**) and [Cd(μ_3-ppda)(μ-pbix)]$_n$ (**14**). The best metal salts to form crystals were acetates, with only **14** prepared from a chloride instead. The reactions yielded crystals in water, DMF or a mixture of the two solvents. In the case of **1**, **3-5** and **12-13**, crystals were obtained following reaction at 120 °C. For **2**, **6-10** and **14** the reaction mixture required heating at a higher temperature to yield crystals. Generally, reactions in water needed to be heated to a higher temperature to give crystals than those in DMF or a water/DMF mix. The reaction between Cd(O_2CMe)$_2$, H_2mpda and mbix only yielded crystals using microwave irradiation, and in this case only a small quantity of product was isolated.

Compounds **3** and **4** are both networks based on zinc(II), mpda and mbix. In this case, use of aqueous NaOH gave **3** whereas water/DMF gave **4**. The two compounds differ in the dimensionality of their networks (see later). Compounds **9** and **10** are both networks based on

cadmium(II), mpda and obix. They were obtained from the same reaction mixture, varying only the time of crystallization. No crystalline products were obtained from the reactions between zinc(II), H_2opda and either obix or pbix, nor from the reactions between cadmium(II), H_2mpda and pbix.

{[Zn(μ-opda)(μ-mbix)]·0.5H_2O}$_n$ (1)

Crystals of compound **1** were obtained from the reaction of zinc(II) acetate with H_2opda and mbix in DMF/water at 120 °C. The asymmetric unit of **1** consists of two half-occupancy zinc(II) centers, one mbix ligand, two half opda ligands and one half non-coordinated water molecule, giving a formula of {[Zn(μ-opda)(μ-mbix)]·0.5H_2O}$_n$ (Fig. S1). Each Zn(II) center is located on a center of symmetry and is coordinated by two nitrogen atoms from two different mbix ligands and two oxygen atoms from two different opda ligands, thus showing distorted tetrahedral coordination geometry. Pairs of mbix ligands bridge the two zinc(II) centers to form Zn_2(mbix)$_2$ dimers (Fig. 1a), which contain 24-membered rings, with a Zn1···Zn2 separation of 9.643 Å. The mbix ligand adopts asymmetric cis-conformation with the dihedral angle between two imidazole rings being 86.92(14)°. There are two kinds of independent opda linker, both of which exhibit symmetrical trans-conformation with angles around the methylene carbons of 117.5(4)° and 115.93(4)°. The opda linker containing O1 and O2 links the dimers into chains running along the *c* axis, whereas that containing O3 and O4 links the dimers into chains running along the *b* axis. Taken together, this leads to the formation of a 2D network (Fig. 1b) with Schlafli vertex symbol of {8^2.10} (Fig. 1c). Neighbouring sheets interdigidate, and interact with each other to form a 3D supramolecular network through C-H···O hydrogen bonds and π···π interactions involving the imidazole rings on the mbix ligands.

{[Zn(μ-mpda)(μ-obix)]·H_2O}$_n$ (2)

Crystals of compound **2** were obtained from the reaction of zinc(II) acetate with H_2mpda and obix in water at 170 °C. The asymmetric unit of **2** consists of one zinc(II) center, one obix ligand, one mpda ligand and one non-coordinated water molecule, giving a formula of {[Zn(μ-mpda)(μ-obix)]·H_2O}$_n$ (Fig. S2). The Zn(II) ion is coordinated by two nitrogen atoms from two different obix ligands and two oxygen atoms from two different mpda ligands, thus showing a distorted tetrahedral coordination geometry. The mpda ligand adopts asymmetric cis-conformation with two carboxylate groups, with the angles about the two -CH_2- groups 109.32(12)° and 114.60(12)°. The obix ligand adopts asymmetric trans-conformation with the dihedral angle between two imidazole rings being 74.62(61)°. Both the mpda and obix linkers connect the zinc(II) centers into coordination polymers, with those connected by obix running along the *a* axis, and those linked by mpda at 47.0° to this. Overall, this leads to 2D networks, with Zn1···Zn1^{i} and Zn1···Zn1^{ii} separations of 8.968 Å[43] and 11.063 Å ((i) $x + 1, y, z$; (ii) $x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2$) (Fig. 2a and Fig. 2b). Each Zn(II) center is four-connected with Schlafli vertex symbol of $\{4^4.6^2\}$. The included water molecules interact through O–H···O hydrogen bonds with mpda carboxylate groups and C–H···O hydrogen bonds with obix imidazole groups.

{[Zn_2(μ-mpda)$_2$(μ-mbix)$_2$]·5H_2O}$_n$ (3)

Crystals of compound **3** were obtained from the reaction of zinc(II) acetate with H_2mpda, mbix and sodium hydroxide in water at 120 °C. The asymmetric unit consists of two Zn(II) centers, two mbix ligands, two mpda ligands and five non-coordinated water molecules, leading to a formula of {[Zn_2(μ-mpda)$_2$(μ-mbix)$_2$]·5H_2O}$_n$ (Fig. S3). Each Zn(II) center is coordinated by two nitrogen atoms from two different mbix ligands and two oxygen atoms from two different mpda ligands, thus showing a distorted tetrahedral coordination geometry. Each mpda ligand adopts asymmetric cis-conformation with two carboxylate groups, and the angles of two -CH_2- range between 114.2(3)° and 116.8(2)°. The Zn(II) ions and mbix ligands produce Zn_2(mbix)$_2$

dimers, with the Zn···Zn separation 11.832 Å. The combination of $Zn_2(mbix)_2$ dimers and mpda ligands produces 1D coordination polymers running parallel to the [101] direction, with a Zn1···Zn2 separation of 10.08 Å (Fig. 3). These coordination polymers are nanotubular in topology, and contain water molecules inside, which form hydrogen bonds with each other and with the carboxylate oxygen atoms. The nanotubes are not completely open, however, as π···π interactions involving the imidazole rings serve to pinch them closed. Further O–H···O hydrogen bonds involving the water molecules link the coordination polymers together.

$\{[Zn(\mu\text{-mpda})(\mu\text{-mbix})]\cdot 2H_2O\}_n$ (4)

Crystals of compound **4** were obtained from the reaction of zinc(II) acetate with H_2mpda and mbix in DMF/water at 120 °C. The asymmetric unit of **4** consists of one Zn(II) center, one mbix ligand, one mpda ligand and two non-coordinated water molecules, giving a formula for **4** of $\{[Zn(\mu\text{-mpda})(\mu\text{-mbix})]\cdot 2H_2O\}_n$ (Fig. S4). The Zn(II) center has distorted tetrahedral coordination geometry with two nitrogen atoms from two different mbix ligands and two oxygen atoms from two different mpda ligands. The mpda ligand adopts asymmetric trans-conformation with two carboxylate groups while the mbix ligand adopts asymmetric cis-conformation with the dihedral angle between two imidazole rings being 81.39(22)°. As with **3**, pairs of mbix ligands connect the zinc centers into $Zn_2(mbix)_2$ dimers. However, in the case of **4**, these dimers are connected into 2D sheets by the mpda linkers (Fig. 4a), with Zn···Zn separations 9.950 Å and 12.546 Å. The sheets have a 'brick wall' topology, which can be represented by the Schlafli vertex symbol of $\{6^3\}$ (Fig. 4b). The sheets stack together with significant interdigitation, most notably involving the $Zn_2(mbix)_2$ dimers, which form π···π interactions associated with the imidazole rings.

{[Zn(μ-mpda)(μ-pbix)]·0.5H_2O}$_n$ (5)

Crystals of compound **5** were obtained from the reaction of zinc(II) acetate with H_2mpda and pbix in DMF/water at 120 °C. The asymmetric unit of **5** consists of one Zn(II) center, two half pbix ligands, one mpda ligand and one half non-coordinated water molecule, giving an overall formula of {[Zn(μ-mpda)(μ-pbix)]·0.5H_2O}$_n$ (Fig. S5). The Zn(II) center is coordinated by two nitrogen atoms from two different pbix ligands and two oxygen atoms from two different mpda ligands, thus showing distorted tetrahedral coordination geometry. The mpda ligand adopts asymmetric trans-conformation with two carboxylate groups while the pbix ligand adopts symmetric trans-conformation with two imidazole rings. Both linkers serve to connect the zinc(II) centers into a 3D diamondoid network (Fig. 5a) which has a Schlafli vertex symbol of {6^6} (Fig. 5b) and Zn···Zn distances of 14.258 Å, 15.352 Å and 11.369 Å. These networks are quadruply interpenetrated. O–H···O hydrogen bonds from the included water molecules to the carboxylate oxygen atoms interlink the interpenetrated coordination networks.

[Zn(μ-ppda)(μ-obix)]$_n$ (6)

Crystals of compound **6** were obtained from the reaction of zinc(II) acetate with H_2ppda and obix in water at 170 °C. The asymmetric unit of **6** consists of a Zn(II) center, one obix ligand and two half ppda ligands, giving a formula of [Zn(μ-ppda)(μ-obix)]$_n$ (Fig. S6). Compound **6** has been reported previously[36], so the structure is described only briefly to provide comparison with the other members of the series. The distorted tetrahedral zinc center is coordinated to two nitrogen atoms from obix ligands and two carboxylate oxygen atoms. Pairs of obix ligands link zinc centers into Zn_2(obix)$_2$ dimers, and these are linked into 2D sheets by the bridging ppda ligands (Fig 6a). Each ppda ligands adopts symmetric trans-conformation with two carboxylate groups while the obix ligand adopts asymmetric trans-conformation with two imidazole rings. Adjacent 2D coordination polymers are joined by C–H···O hydrogen bonds to form a 3D supramolecular network.

{[Zn(μ-ppda)(μ-mbix)]·0.5H_2O}$_n$ (7)

Crystals of compound **7** were obtained from the reaction of zinc(II) acetate with H_2ppda and mbix in water at 170 °C. The asymmetric unit of **7** consists of two half-occupancy Zn(II) centers, one mbix ligand, one ppda ligand and one half non-coordinated water molecule, giving an overall formula of {[Zn(μ-ppda)(μ-mbix)]·0.5H_2O}$_n$ (Fig. S7). The Zn(II) center is coordinated by two nitrogen atoms from two different mbix ligands and two oxygen atoms from two different ppda ligands, and shows distorted tetrahedral coordination geometry. The ppda ligand adopts asymmetric trans-conformation while the mbix ligand adopts asymmetric cis-conformation. Zinc(II) centers are linked by pairs of mbix ligands into Zn_2(mbix)$_2$ dimers with a Zn···Zn separation of 9.867 Å. These dimers are connected into 2D sheets by the bridging ppda ligands (Fig. 7a). The sheets have a 'brick wall' type topology, with Schlafli vertex symbol of {6^3} (Fig. 7b) and the formation of 72-membered rings. The mbix ligands protrude from the sheets, and this allows for interdigitation between adjacent sheets, which is facilitated by C–H···O hydrogen bonds between the methylene groups and carboxylate oxygen atoms and π···π interactions involving the benzene rings of the mbix ligands.

{[Zn(μ-ppda)(μ-pbix)]·H_2O·DMF}$_n$ (8)

Crystals of compound **8** were obtained from the reaction of zinc(II) acetate with H_2ppda and pbix in DMF/water at 160 °C. The asymmetric unit of **8** consists of one Zn(II) center, one ppda ligand, one pbix ligand, one DMF molecule and one non-coordinated water molecule giving an overall formula of {[Zn(μ-ppda)(μ-pbix)]·H_2O·DMF}$_n$ (Fig. S8). Both the ppda and pbix ligands adopt asymmetric cis-conformation. Pairs of pbix ligands bridge the zinc(II) centers to generate Zn_2(pbix)$_2$ dimers. These dimers are linked together by pairs of ppda linkers to give 1D chains (Fig. 8). The Zn···Zn distances within the chains are 11.368 Å, for the metal centers bridged by pairs of pbix ligands, and 9.451 Å for the metal centers bridged by pairs of ppda ligands. Both the pbix and ppda ligands adopt cis conformations, with the dihedral angle

between two pbix imidazole rings being 61.16(45)°. Intermolecular C-H···O hydrogen bonds and π···π interactions serve to link the polymer chains into the gross structure.

{[Cd(μ-mpda)(μ-obix)$_{1.5}$]·H$_2$O}$_n$ (9) and {[Cd(μ-mpda)(μ-obix)]·H$_2$O}$_n$ (10)

Crystals of compounds **9** and **10** were obtained from the reaction of cadmium(II) acetate with H$_2$mpda and obix in water at 170 °C, with **9** crystallising on cooling, and **10** appearing after 1 week. The asymmetric unit of **9** consists of one cadmium(II) center, one mpda ligand, one and a half obix ligands and one non-coordinated water molecule (Fig. S9).

The cadmium(II) center in **9** is seven-coordinate, bonding to three nitrogen atoms from three different obix ligands and four oxygen atoms from two different mpda ligands. Thus each carboxylate group is unsymmetrically κ^2-coordinated (Cd(1)–O(1) 2.353(5), Cd(1)–O(2) 2.694(7), Cd(1)–O(3) 2.497(9), Cd(1)–O(4) 2.561(11) Å). The obix ligands interlink the cadmium(II) centers into ladder-like coordination polymers, and these are interconnected into a 2D network by the bridging mpda linkers (Fig. 9a). The mpda ligand adopts an asymmetric cis-conformation with -CH$_2$- angles of 109.7(5)° and 115.2(5)°. The half-occupancy obix ligand adopts symmetric a trans-conformation while the other obix ligand adopts an asymmetric trans-conformation. Overall, the network can be represented by the Schlafli vertex symbol of $\{3^3.4^4.5^3\}$ (Fig. 9b).

The asymmetric unit of **10** consists of one cadmium(II) center, one obix ligand, one mpda ligand and one non-coordinated water molecule (Fig. S10). The coordination geometry of the cadmium(II) center is distorted octahedral, with two nitrogen atoms from two different obix ligands and four oxygen atoms from two different mpda carboxylate groups. Both the mpda and obix ligands adopt asymmetric trans-conformations.

The cadmium(II) centers in **10** are linked by the obix ligands into coordination polymers running parallel to the [100] direction, with a Cd···Cd separation of 11.240 Å. These chains are cross-linked by the mpda ligands, which in isolation give coordination polymers running parallel to

the [010] direction, with a Cd···Cd separation of 11.800 Å. The combination of the two coordination polymers leads to corrugated 2D sheets with the Schlafli vertex symbol of $\{4^4.6^2\}$, which are shown in Fig. 10a. Neighbouring sheets are interpenetrated, and this gives rise to a 3D structure (Fig. 10b and Fig. 10c).

$\{[Cd(\mu\text{-mpda})(\mu\text{-mbix})(H_2O)]\cdot H_2O\}_n$ (11)

Crystals of compound **11** were obtained from the reaction of cadmium(II) acetate with H_2mpda and mbix in water under microwave radiation for 30 minutes. The asymmetric unit of **11** consists of one cadmium(II) center, one mbix ligand, one mpda ligand, one coordinated water molecule and one non-coordinated water molecule (Fig. S11). The cadmium(II) center is coordinated to two nitrogen atoms from two different mbix ligands, four oxygen atoms from two different mpda carboxylate groups and an oxygen atom from the water molecule. This gives a coordination number of 7 and approximate pentagonal bipyramidal geometry. The mbix and mpda ligands both adopt asymmetric trans-conformations. Pairs of mbix ligands connect the cadmium(II) centers into $Cd_2(mbix)_2$ dimers, similar to those in the zinc compounds **1**, **3**, **4** and **7**. The inclusion of a water molecule within the cadmium coordination spheres allows the dimers to be further bound together by O–H···O hydrogen bonds, leading to a Cd···Cd separation of 6.170 Å. Adjacent $Cd_2(mbix)_2$ dimers are inter-linked by mpda ligands, generating a 2D coordination network with a Cd···Cd separation of 10.851 Å (Fig. 11a and Fig. 11b). Neighbouring sheets interdigitate, with π···π interactions between imidazole rings the most significant intermolecular interactions.

$[Cd(\mu_3\text{-ppda})(\mu\text{-obix})]_n$ (12), $[Cd(\mu_3\text{-ppda})(\mu\text{-mbix})]_n$ (13) and $[Cd(\mu_3\text{-ppda})(\mu\text{-pbix})]_n$ (14)

Crystals of compounds **12-13** were obtained from the reaction of cadmium(II) acetate with H_2ppda and either obix or mbix in DMF/water at 120 °C. Crystals of compound **14** were obtained from the reaction of cadmium(II) chloride with H_2ppda and pbix in DMF at 140 °C. The structures of **12-14** are very similar, hence can be treated together. The asymmetric units of **12-14** contain one cadmium(II) center, one bix ligand (obix in **12**, mbix in **13** and pbix in **14**) and one ppda ligand (Figs. S12–S14). Each cadmium(II) center is coordinated by two nitrogen atoms from two different bix ligands and five oxygen atoms from three different ppda ligands. Each ppda ligand adopts asymmetric trans-conformation with two bidentate-chelating carboxylate groups. This connects the cadmium(II) centers into $Cd_2(O_2CR)_4N_4$ secondary building units, which are inter-linked by pairs of bix ligands into 1D coordination polymers that are cross-linked by the ppda linkers into 2D coordination networks. The structures of **12-14** are shown in Figs. 12-14. The ppda ligands in **12-14** all adopt asymmetric trans-conformations. In **13** and **14**, each mbix or pbix ligand adopts an asymmetric trans-conformation while the obix ligand in **12** adopts an asymmetric cis-conformation. The Cd···Cd distance bridged by the bix linker is 13.840 Å for **12**, 15.631 Å for **13** and 15.289 Å for **14**, whereas the Cd···Cd distance bridged by ppda ranges from 9.858 Å to 10.062 Å.

Discussion

In total, 14 zinc or cadmium compounds containing a bis(imidazol-1-ylmethyl)benzene (bix) and a phenylenediacetate (pda) ligand have been prepared and structurally characterised. The compounds contain one of three structural isomers of bix (obix = 1,2-bis(imidazol-1-ylmethyl)benzene, mbix = 1,3-bis(imidazol-1-ylmethyl)benzene, pbix = 1,4-bis(imidazol-1-ylmethyl)benzene) and one of three structural isomers of pda (opda = 1,2-phenylenediacetate, mpda = 1,3-phenylenediacetate, ppda = 1,4-phenylenediacetate). All 14 compounds have been shown by X-ray crystallography to form coordination polymer/network structures.

Of the eight compounds based on zinc, all have structures in which individual zinc(II) centers act as nodes. In all cases the zinc(II) centers have distorted tetrahedral geometry and are coordinated to two nitrogen atoms from bix ligands and two carboxylate oxygen atoms from pda ligands. N–Zn–N angles range from 102.7° to 112.4°, whereas O–Zn–O angles have a far greater range, from 93.3° to 131.8°. This parameter occurs alongside variation in the Zn···O distances involving non-coordinated oxygen atoms, which range from 2.798 Å to 3.033 Å.

Six of the eight zinc compounds contain $M_2(bix)_2$ dimers, in which pairs of bix ligands bridge between pairs of zinc(II) centers. Having a pair of linkers between two nodes effectively reduces the connectivity of the nodes in the networks from four to three. These $M_2(bix)_2$ dimers occur in all four compounds containing mbix, in addition to one of the two compounds containing either obix or pbix. This clearly demonstrates that all of the isomers of bix are capable of forming these dimers. Moreover, dimers can form with the bix ligands either in cis or trans conformations. Thus while **1**, **4**, **7** and **8** contain cis mbix or pbix ligands, obix, mbix and pbix are also capable of forming networks when in the trans conformation, and indeed obix and mbix can form $M_2(bix)_2$ dimers while in the trans conformation.

Most of the zinc(II) coordination polymers observed form two-dimensional networks, with five of the eight compounds complying with this. In contrast, two compounds (**3** and **8**) form one-dimensional polymers whereas one (**5**) forms an interpenetrated three-dimensional structure. The products are formed using different temperatures (120 °C to 170 °C) and solvents, but there appears to be no link between the reaction conditions and the product dimensionality.

The one- and two-dimensional polymers are cross-linked by C–H···O hydrogen bonds and π···π interactions, with in many cases some degree of inter-digitation observed, which serves both the maximise the intermolecular interactions and minimise the free space available. Seven of the eight compounds contain included solvent molecules.

Six cadmium(II) compounds containing bix and pda ligands have been structurally characterised. In all six crystal structures, the cadmium(II) center has a higher coordination

number than four, reflecting the larger size of cadmium(II) than zinc(II). The six compounds all form two-dimensional coordination networks. In three of the compounds (**9-11**), the nodes are made up from single cadmium(II) centers, whereas the remaining three (**12-14**) have nodes that are $Cd_2(O_2CR)_4N_4$ dimers.

Only one of the six cadmium(II) compounds (**11**) has a structure featuring $M_2(bix)_2$ dimers, perhaps reflecting the greater flexibility of cadmium chemistry, with the higher coordination numbers and dimeric secondary building units imparting greater structural diversity. The Cd···Cd distance in **11** is shorter than the Zn···Zn distance in any of the compounds containing $Zn_2(bix)_2$ dimers. The cadmium(II) centers contain coordinated water molecules, and intramolecular O–H···O hydrogen bonds involving these and carboxylate oxygen atoms lock the dimer into position, and shorten the Cd···Cd distance.

The bix and pda ligands display a range of conformations in the products characterised. The mbix, pbix, mpda and ppda ligands all show examples of both cis and trans geometries. In contrast, obix and opda only show trans conformations, which is likely to be a consequence of the cis conformations being sterically disfavoured.

3.2. Powder X-ray Diffraction (PXRD), Photoluminescence and Thermal Properties

The experimental PXRD patterns of the complexes **1-14** agreed with simulated patterns from their single-crystal structures to confirm the phase purity of the complexes at room temperature (Figs. S15–S25).

The photoluminescent properties of phenylenediacetic acid isomers and complexes **1–14** at room temperature were determined. As illustrated in Figs. S26, the intense broad emissions peaks appeared at 380 nm (λ_{ex}=292 nm) for **2**, 345, 365 and 379 nm (λ_{ex}=292 nm) for **3**, 343, 361 and 380 nm (λ_{ex}=292 nm) for **4**, 450 nm (λ_{ex}=292 nm) for **7**, 381 nm (λ_{ex}=292 nm) for **8**, 380 and 450 nm (λ_{ex}=292 nm) for **9**, 380 nm (λ_{ex}=346 nm) for **13** and 403 nm (λ_{ex}=292 nm) for **14**. For free organic ligands, the emissions were observed at 387 nm (λ_{ex}=292 nm) for opda and

mpda, 484 nm (λ_{ex}=335 nm) for ppda. Complexes **1**, **5**, **10**, **11** and **12** showed very weak emissions at room temperature, so their emission spectra have not been included. The emissions for complexes are neither metal-to-ligand charge transfer (MLCT) nor ligand to metal transfer (LMCT), since the Zn(II) and Cd(II) ions are difficult to oxidize or reduce, and are likely attributed to the intraligand $\pi\rightarrow\pi^*$ or $\pi\rightarrow$n transitions [60]. Similar emission bands in the region of 350-450 nm for other d^{10} metal coordination polymers with pda ligands were observed.

The framework stabilities and thermal decomposition behaviors of complexes **1-14** were investigated through thermogravimetric analysis techniques in a static air atmosphere in the temperature range 30–700 ^{o}C, as shown in Fig. S27. The TG study of **1** shows an initial weight loss of 1.7% (1.8% calcd) in 30-271 °C range, suggesting the loss of half lattice water and then the anhydrous compound starts to decompose. For **2**, the first weight loss in the temperature range of 30−130 °C is consistent with the removal of lattice water molecules (obsd 3.1%, calcd 3.5%) and further weight loss was observed at about 130-569 °C, which could be attributed to the decomposition of the organic components (obsd 79.1%, calcd 80.7%). For **4**, the 7.1% mass loss observed between 30 and 143 ºC corresponds to the loss of two lattice water molecule (calculated 6.8%), the second weight loss observed between 143 and 372 ºC corresponds to the decomposition of mbix (obsd 44.8%, calcd 44.8%) and the third weight loss observed between 372 and 510 ºC corresponds to the decomposition of mpda (obsd 36.7%, calcd 33.1%). Compound **7** releases solvent water in 30-99 °C. After 281 °C, the anhydrous compound starts to decompose.

The decomposition of **9** proceeds in four steps and the first weight loss in the temperature range of 30–260 °C is consistent with the removal of one lattice water molecule (obsd 4.0%, calcd 2.6%). After 260 °C, the anhydrous compound starts to decompose. Compound **10** releases one uncoordinated water molecules in 77-205 °C (obsd 2.8%, calcd 3.6%). The anhydrous compound is stable to 283 °C, and then starts to decompose. Complex **12** is stable up to 124 ^{o}C then it starts to decompose, with this proceeding in six steps.

Conclusions

A series of zinc(II) and cadmium(II) coordination polymers with semi-rigid neutral bix and anionic pda ligands have been synthesized and structurally characterized. Systematic variation of the positions of the donor groups on the bix and pda ligands has been carried out, and the structural analyses reveal that the majority of the compounds form 2D coordination networks, though 1D coordination polymers and a 3D network have also been observed. The eight zinc(II) compounds contains more structural features in common that their cadmium(II) analogues, with the coordination number four in all cases, and six of the compounds containing $M_2(bix)_2$ dimers. In contrast, the greater size of the cadmium(II) center leads to greater flexibility in the coordination sphere, however, the three cadmium-ppda compounds give isoreticular structures. The photoluminescence of the complexes may originate from the o/m/ppda intraligand fluorescence since the Zn(II) ions and Cd(II) ions are difficult to oxidize or reduce because of the d^{10} configuration.

Acknowledgements

This work has been supported by The Scientific and Technological Research Council of Turkey (TUBITAK, No: 1649B031402373) and the Research Fund of Eskişehir Osmangazi Üniversitesi –Turkey by project Number: 201519029.

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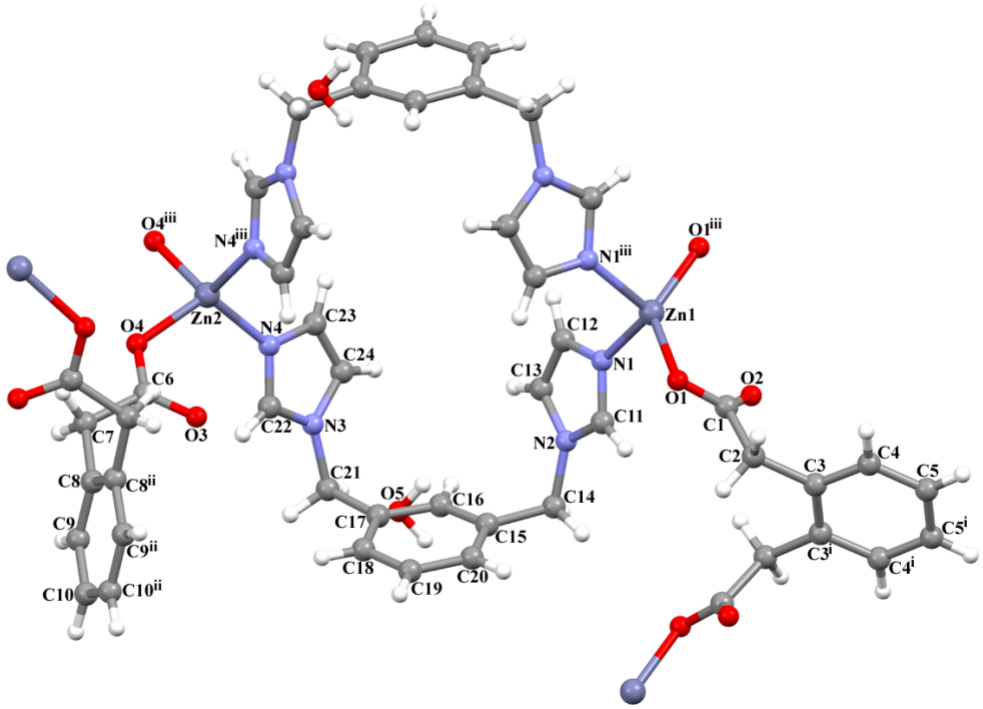
Table 1. Crystal data and structure refinement parameters for complexes **1-7**

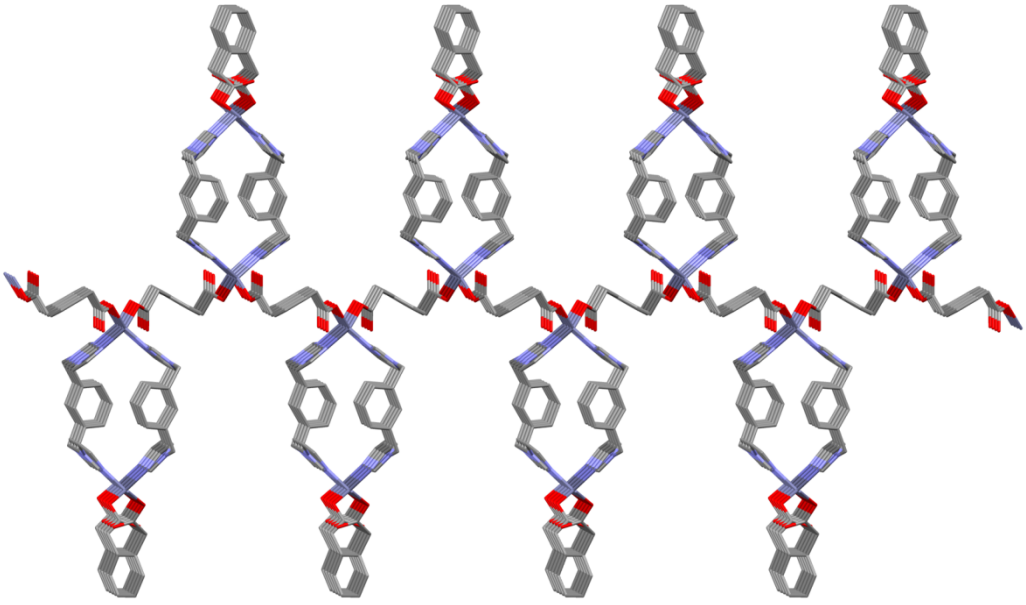
Crystal data	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Empirical formula	$C_{96}H_{92}N_{16}O_{17}Zn_4$	$C_{24}H_{24}N_4O_5Zn$	$C_{48}H_{54}N_8O_{13}Zn_2$	$C_{24}H_{26}N_4O_6Zn$	$C_{48}H_{46}N_8O_9Zn_2$	$C_{24}H_{22}N_4O_4Zn$	$C_{48}H_{46}Zn_2N_8O_9$
Formula weight	2003.34	513.84	1081.73	531.86	1009.67	495.82	1009.67
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	Pnna	$P2_1/n$	P-1	C2/c	C2/c	P-1	C2
a (Å)	41.5499 (10)	11.0631 (4)	13.6206 (3)	15.131 (5)	19.2996 (4)	9.8416 (3)	14.4485 (13)
b (Å)	13.3577 (4)	16.6340 (7)	14.3122 (3)	24.945 (4)	21.5798 (4)	9.9615 (3)	25.5197 (19)
c (Å)	8.1361 (2)	12.8558 (5)	14.4855 (4)	16.053 (5)	14.0145 (3)	13.5652 (4)	8.2397 (7)
α (º)	90.00	90.00	97.033 (1)	90.00	90.00	70.333 (1)	90.00
β (º)	90.00	93.940 (2)	100.4150 (11)	103.963 (5)	128.843 (1)	69.0200 (9)	113.192 (4)
γ (º)	90.00	90.00	110.270 (1)	90.00	90.00	73.704 (1)	90.00
V (Å^3)	4515.6 (2)	2360.18 (16)	2552.34 (11)	5880 (3)	4546.07 (17)	1149.74 (6)	2792.6 (4)
Z	2	4	2	8	4	2	2
D_c (g cm^{-3})	1.473	1.446	1.408	1.202	1.475	1.432	1.201
μ (mm^{-1})	1.13	1.08	1.01	0.87	1.12	1.11	0.91
θ range (º)	2.5-21.3	2.2-31.3	2.7-26.2	2.3-25.9	2.7-32.9	3.4-29.7	3.1-27.1
Measured refls.	13418	31440	69069	28906	34610	33256	8975
Independent refls.	3188	8989	18659	5657	8736	8839	5428
R_{int}	0.055	0.026	0.045	0.044	0.019	0.030	0.033
S	1.03	1.04	0.96	1.36	1.06	1.04	1.11
R1/wR2	0.043/0.096	0.036/0.098	0.051/0.161	0.117/0.367	0.034/0.096	0.041/0.102	0.064/0.217
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	0.25/-0.28	0.41/-0.26	1.21/-0.63	1.92/-2.35	0.38/-0.21	0.44/-0.25	1.17/-0.41

Table 2. Crystal data and structure refinement parameters for complexes **8-14**

Crystal data	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Empirical formula	$C_{27}H_{31}ZnN_5O_6$	$C_{31}H_{31}CdN_6O_5$	$C_{24}H_{24}CdN_4O_5$	$C_{24}H_{26}CdN_4O_6$	$C_{24}H_{22}CdN_4O_4$	$C_{24}H_{22}CdN_4O_4$	$C_{24}H_{22}CdN_4O_4$
Formula weight	586.94	680.02	560.87	578.89	542.86	542.86	542.86
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	C2/c	$P2_1/n$	$P2_1/n$	P-1	P-1	P-1
a (Å)	9.7223 (6)	24.287 (2)	11.2405 (6)	9.5126 (11)	10.4017 (13)	11.092 (5)	9.7719 (1)
b (Å)	12.2311 (6)	14.3356 (12)	17.3127 (9)	17.166 (2)	11.4518 (14)	11.359 (5)	11.4305 (1)
c (Å)	12.6053 (7)	18.4717 (16)	12.0543 (7)	15.639 (2)	11.4624 (14)	11.416 (5)	11.6532 (1)
α (º)	103.038 (2)	90.00	90.00	90.00	118.937 (5)	86.677 (5)	60.879 (1)
β (º)	95.238 (3)	109.217 (3)	91.120 (2)	106.033 (4)	101.621 (5)	61.771 (6)	74.7830 (11)
γ (º)	105.139 (2)	90.00	90.00	90.00	97.777 (6)	66.842 (5)	74.863 (1)
V (Å^3)	1391.53 (14)	6072.9 (9)	2345.4 (2)	2454.3 (5)	1126.4 (2)	1150.5 (9)	1083.41 (2)
Z	2	8	4	4	2	2	2
D_c (g cm^{-3})	1.401	1.488	1.588	1.567	1.601	1.567	1.664
μ (mm^{-1})	0.93	0.77	0.97	0.94	1.01	0.99	1.05
θ range (º)	3.2-28.3	3.1-28.3	3.4-28.3	3.0-28.3	2.5-23.8	2.2-27.1	2.6-30.0
Measured refls.	55151	23211	47351	13740	12101	18988	19223
Independent refls.	5171	5853	5803	4793	3435	5057	4247
R_{int}	0.091	0.046	0.022	0.058	0.029	0.045	0.027
S	1.12	1.19	1.15	1.08	1.11	1.09	1.06
R1/wR2	0.074/0.214	0.062/0.153	0.034/0.089	0.061/0.171	0.032/0.083	0.038/0.081	0.027/0.064
$\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	1.97/-0.66	1.01/-1.14	1.13/-0.89	2.40/-2.10	0.76/-0.52	0.63/-0.81	0.55/-0.48


O4iii
N4iii
O4
Zn2
N4
C23
C24
C6
C7
O3
C22
N3
C8
C8ii
C21
O5
C16
C14
C9
C17
C15
C9ii
C18
C19
C20
C10
C10ii
O1iii
N1iii
Zn1
C12
N1
C13
O1
O2
C11
C1
N2
C2
C3
C4
C5
C5i
C3i
C4i

(a)



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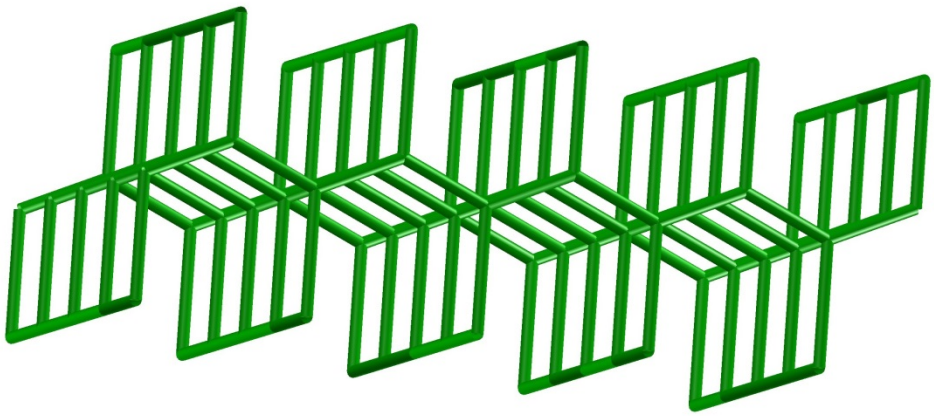
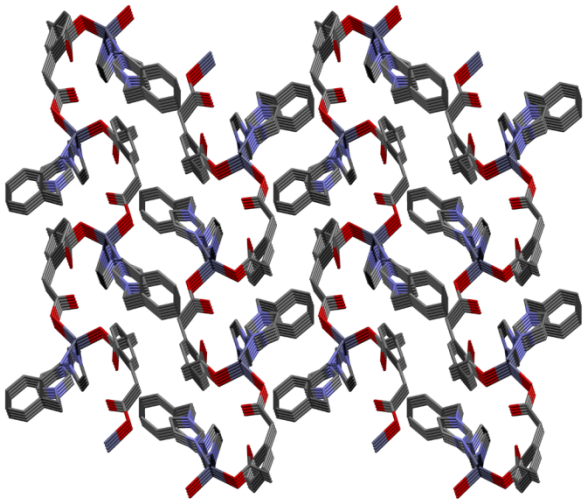
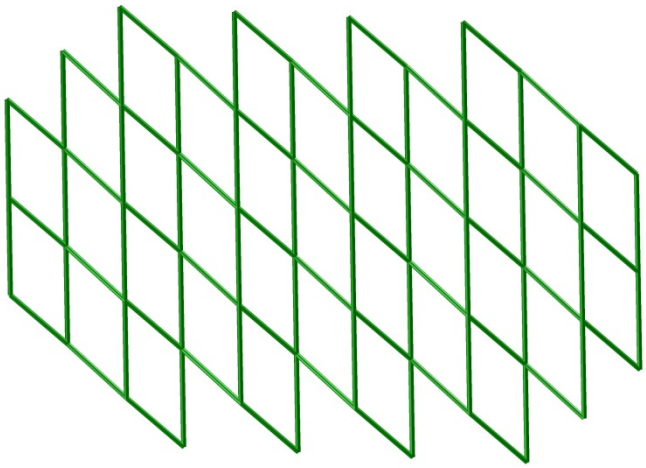


(c)

Fig. 1. The structure of **1**, showing (a) the $Zn_2(mbix)_2$ dimer, (b) part of an infinite 2D layer, (c) the 2D topological network.



(a)



(b)

Fig. 2. The structure of **2**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.

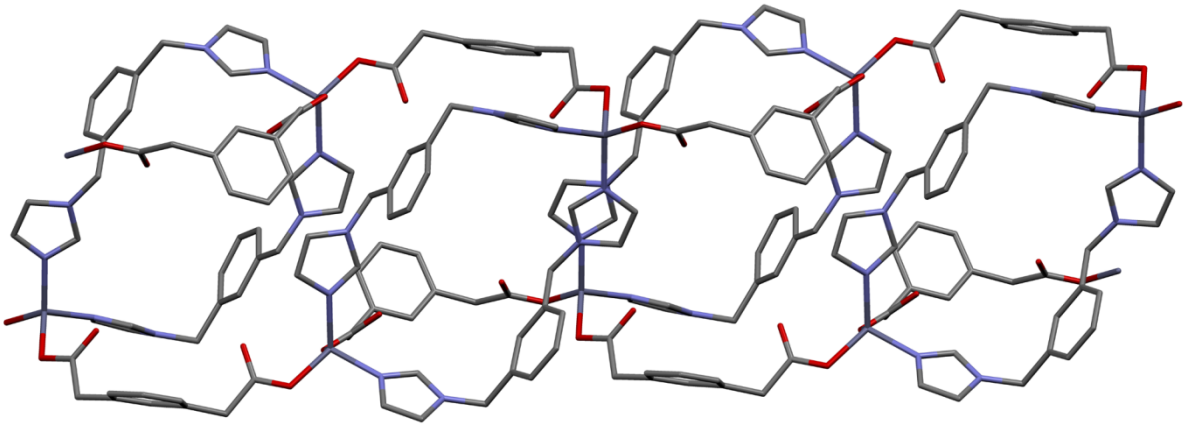
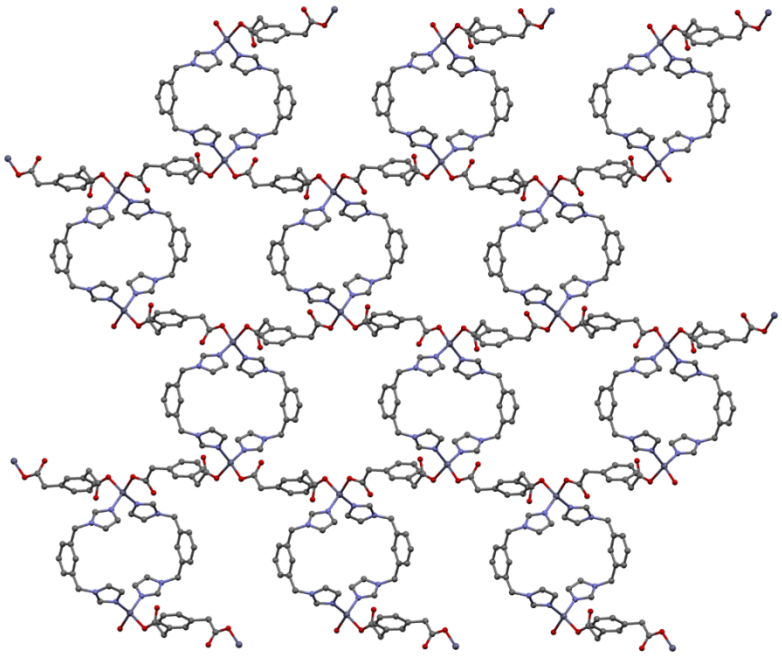
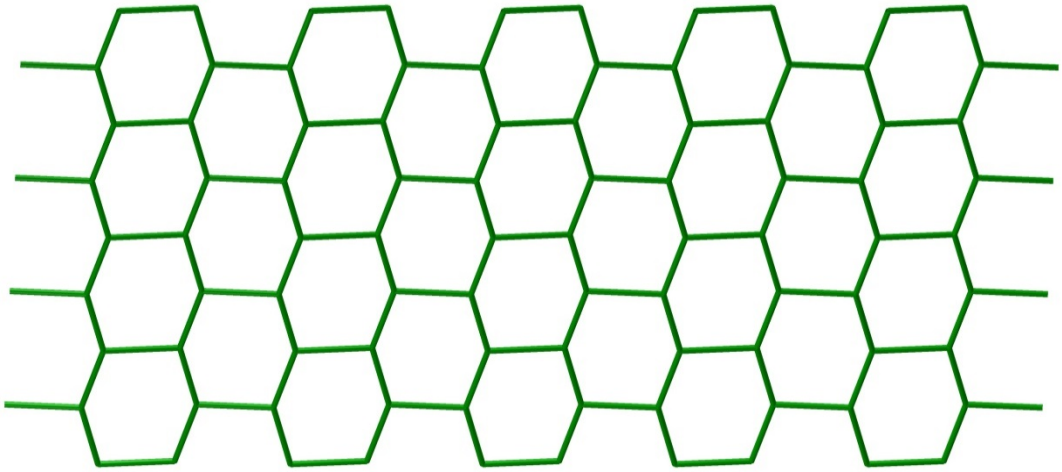


Fig. 3. Part of one of the nanotubes present in the structure of **3**.

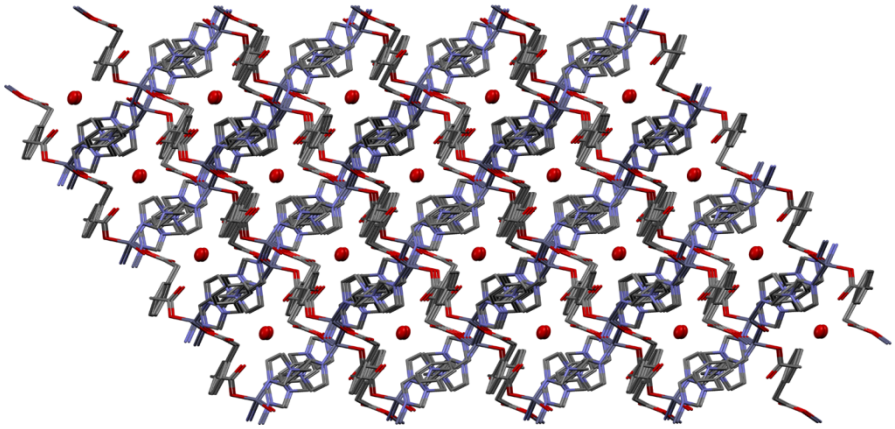


(a)

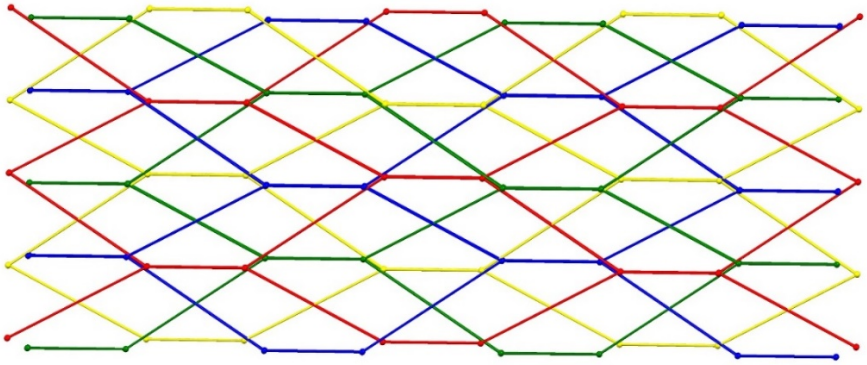


(b)

Fig. 4. The structure of **4**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.

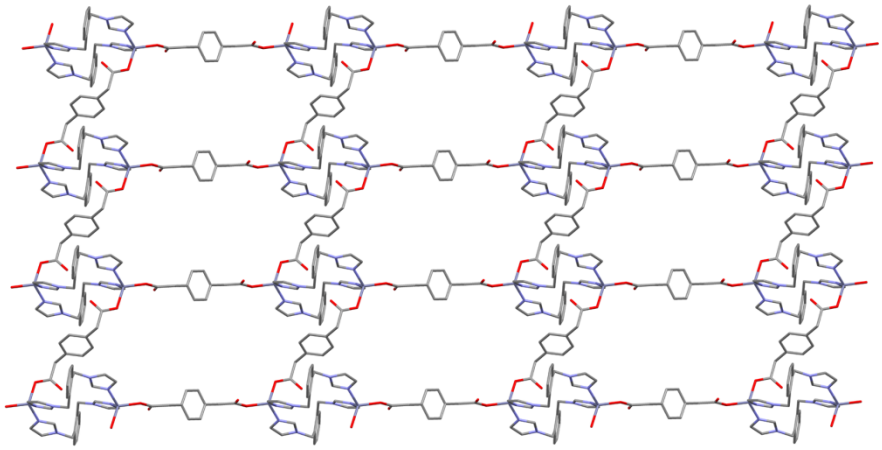


(a)

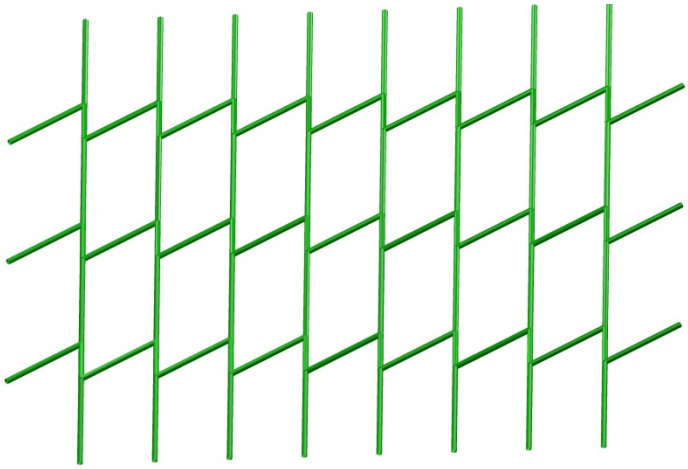


(b)

Fig. 5. The structure of **5**, showing (a) the interpenetrated 3D network, and (b) a topological representation of this.

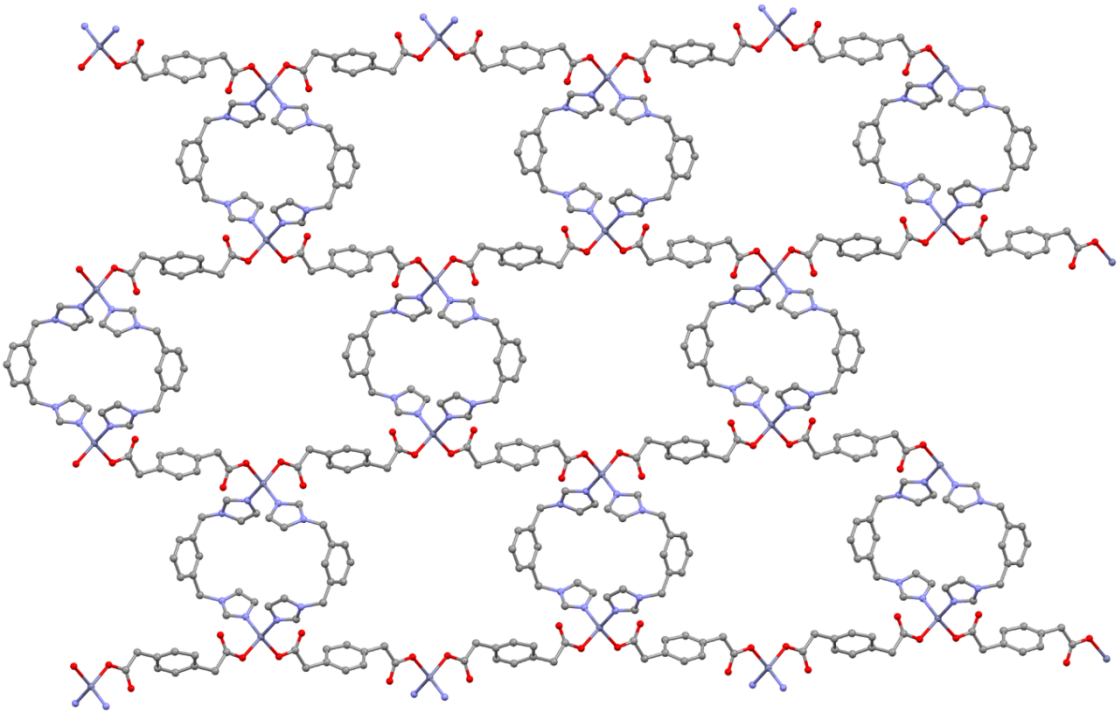


(a)

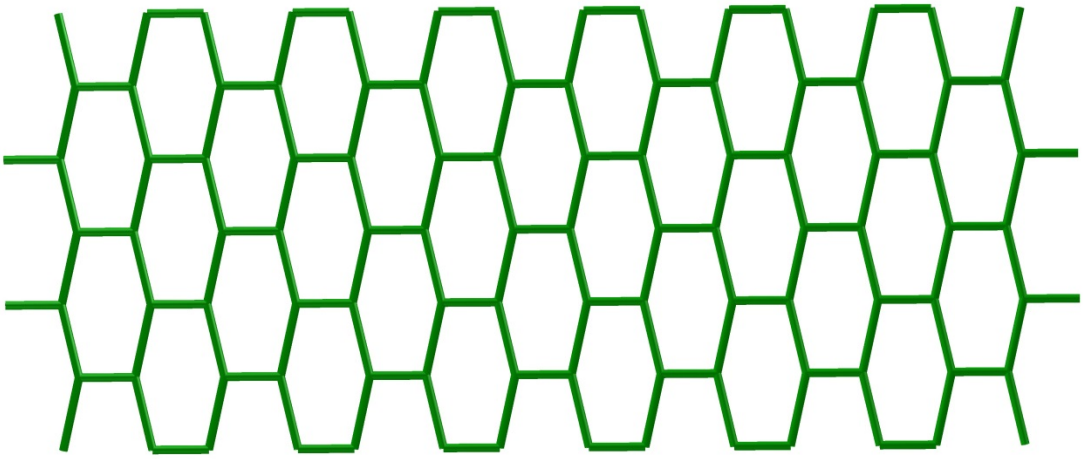


(b)

Fig. 6. The structure of **6**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.



(a)



(b)

Fig. 7. The structure of **7**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.

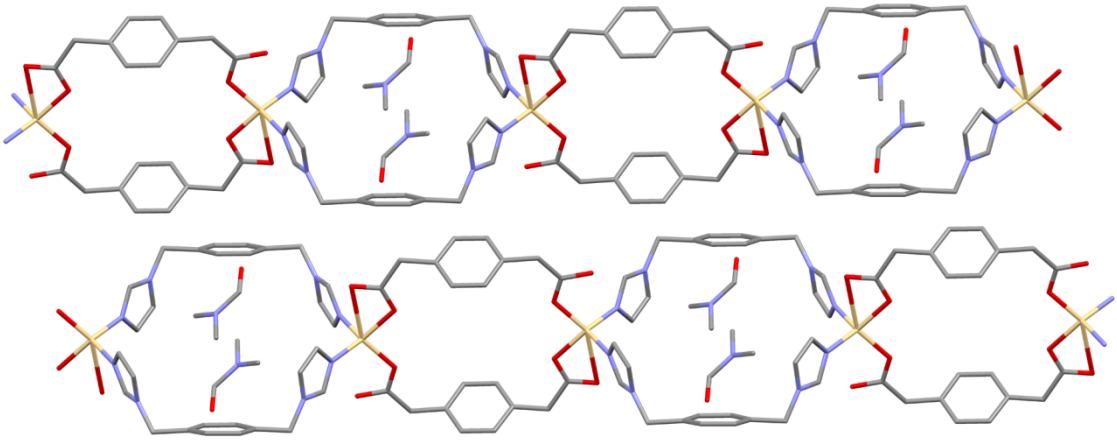
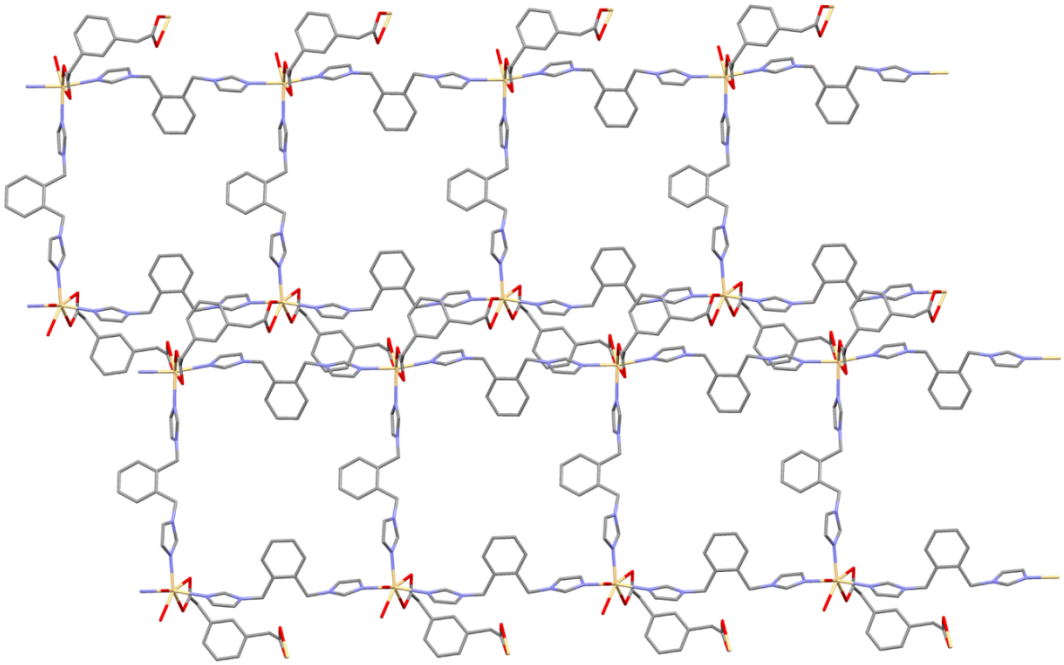


Fig. 8. The structure of **8**, showing two parallel 1D polymers.



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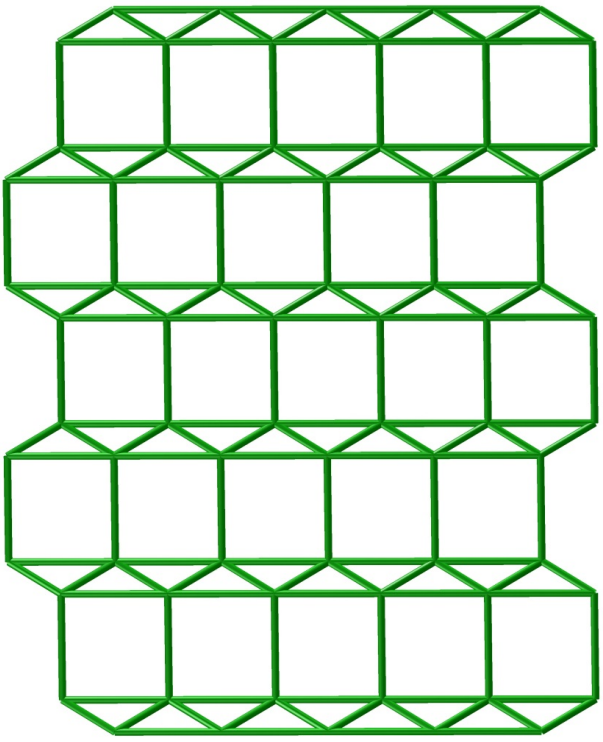
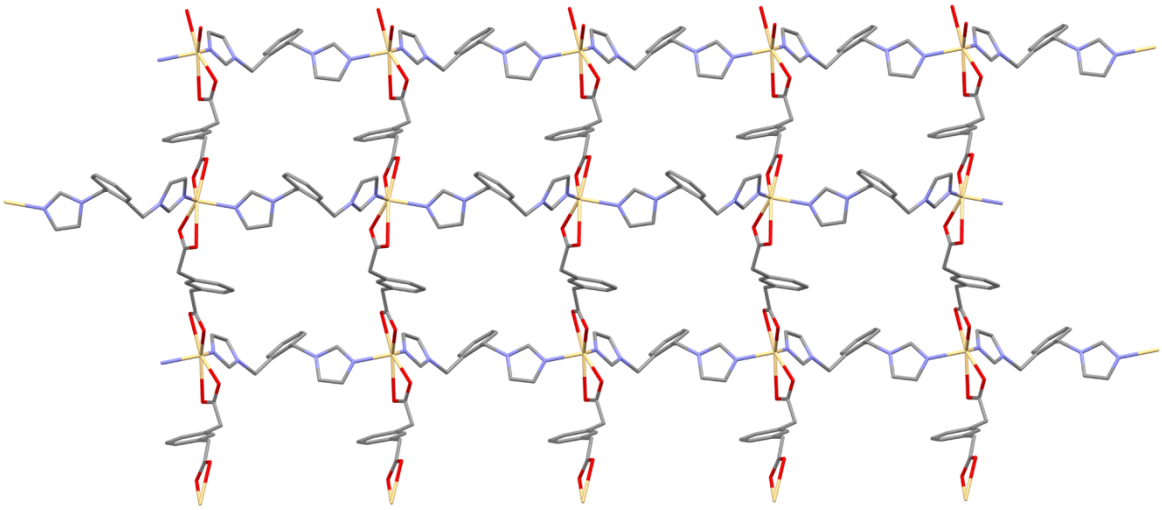


(b)

Fig. 9. The structure of **9**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.



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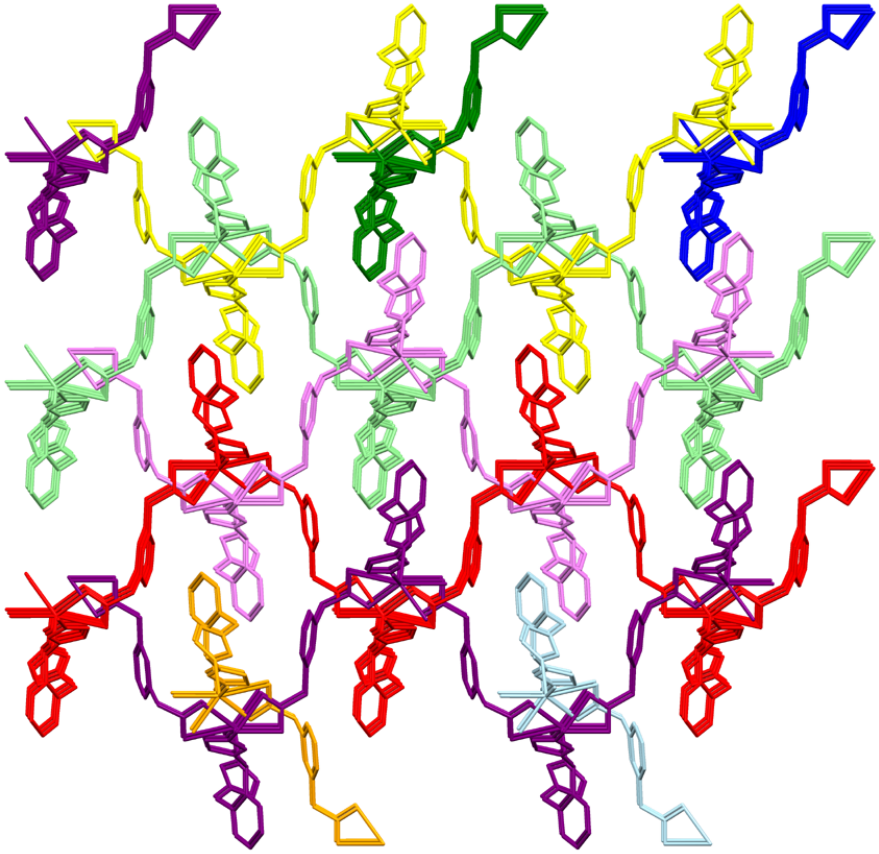

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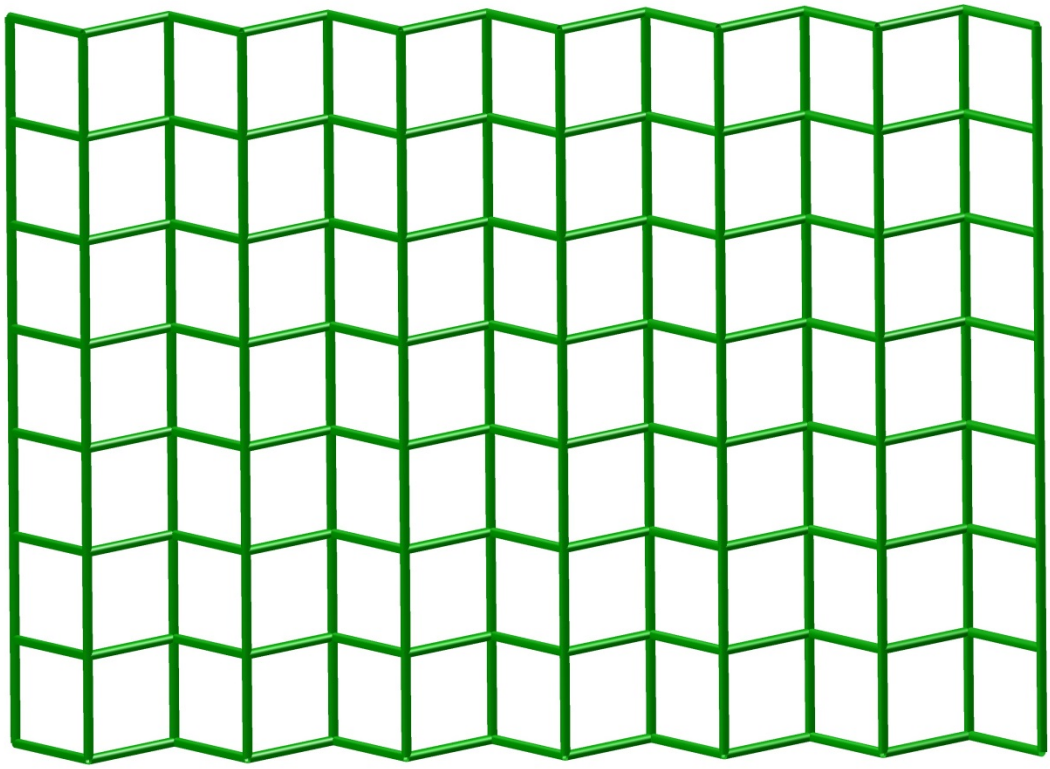
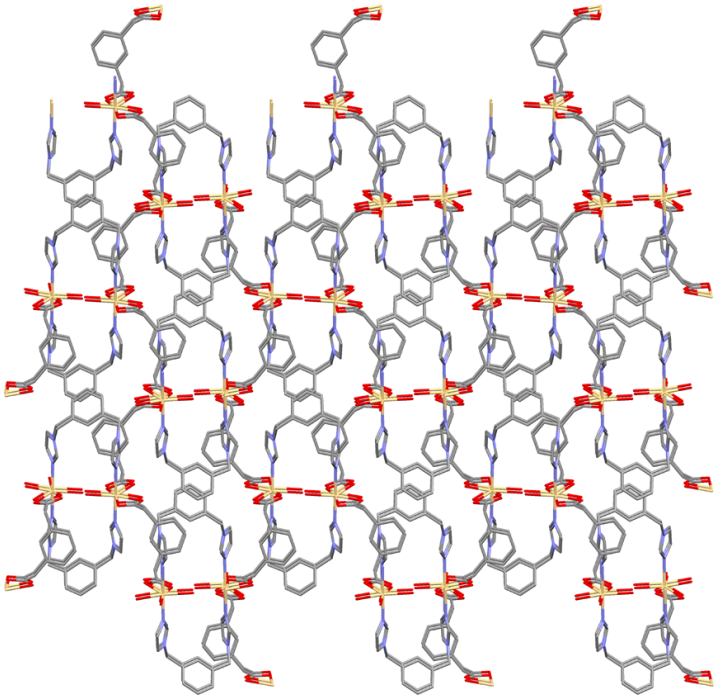
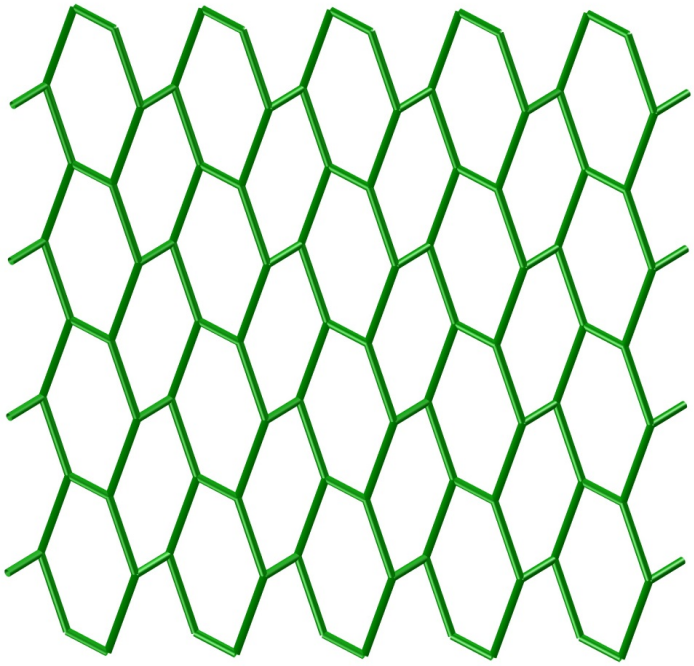


(c)

Fig. 10. The structure of **10**, showing (a) part of an infinite 2D layer, (b) interpenetration of the layers into a 3D structure, and (c) the 2D topological network.

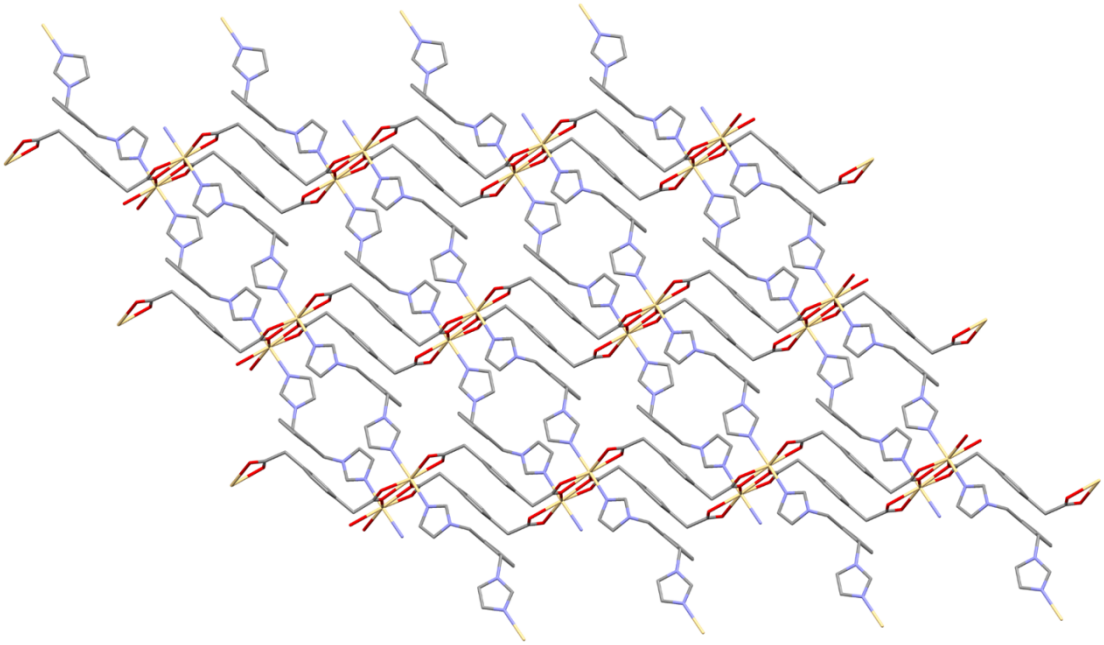


(a)



(b)

Fig. 11. The structure of **11**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.



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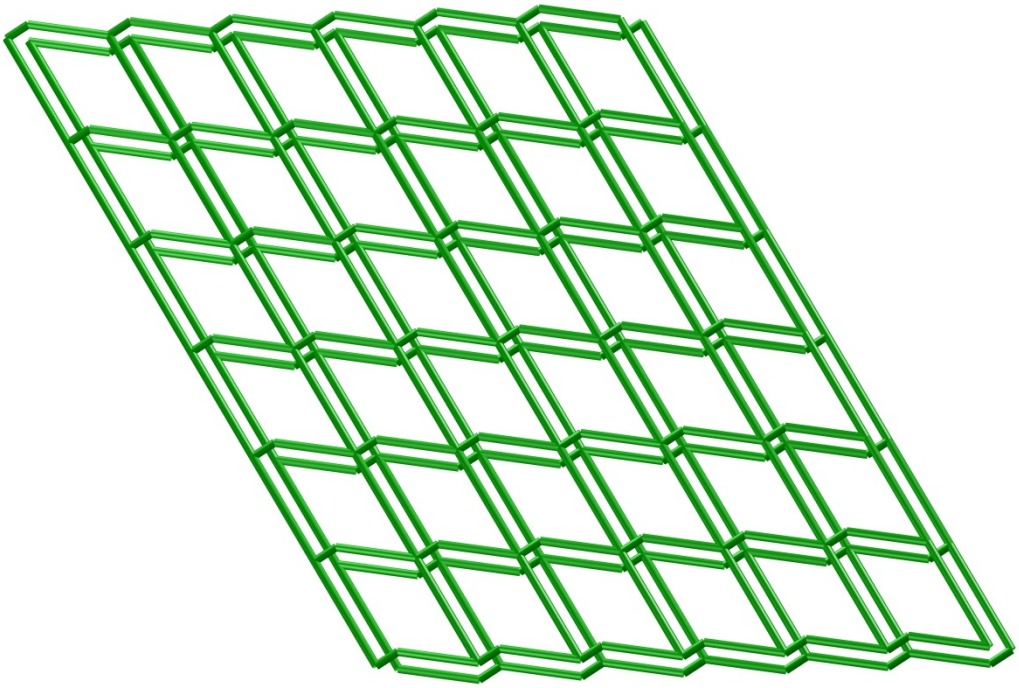
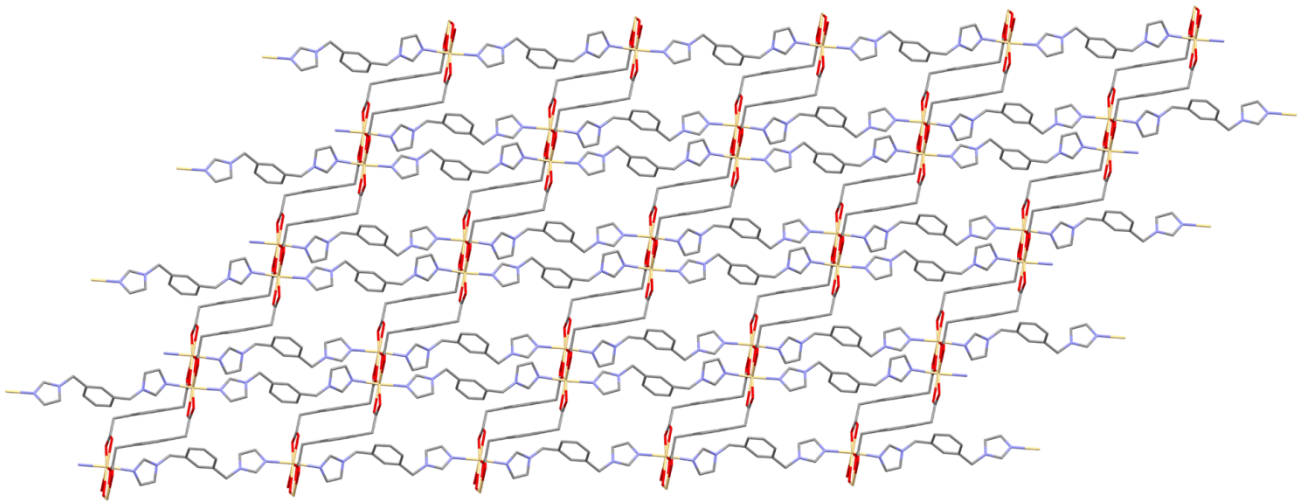


(b)

Fig. 12. The structure of **12**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.



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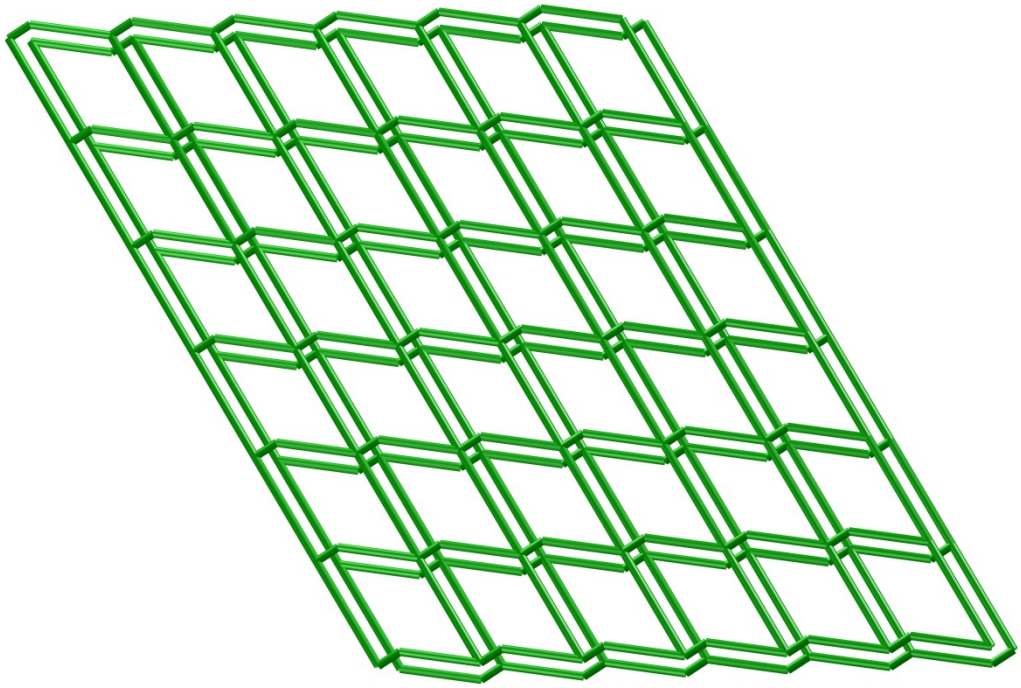
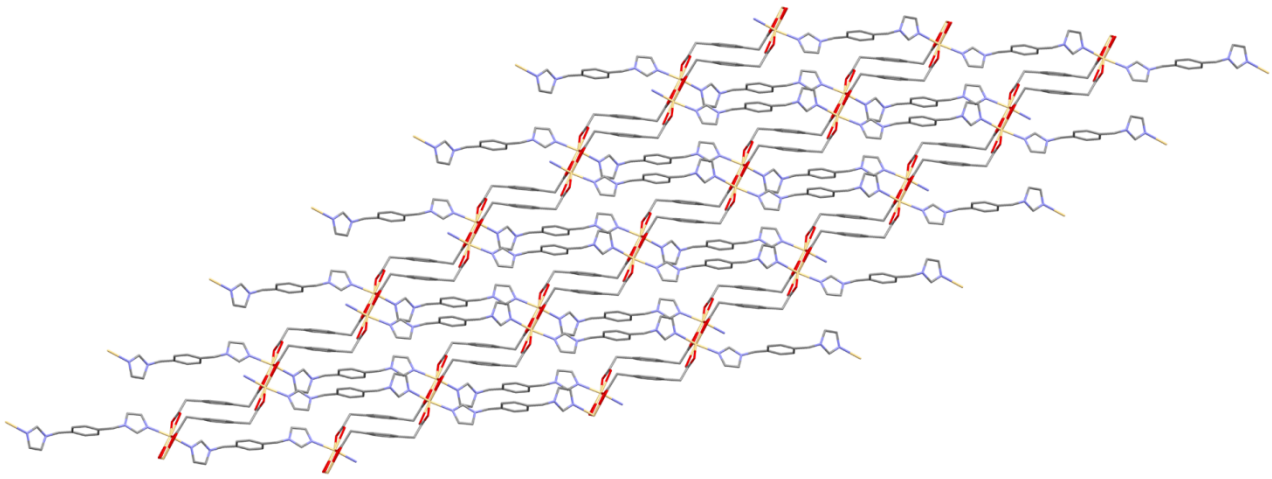


(b)

Fig. 13. The structure of **13**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.



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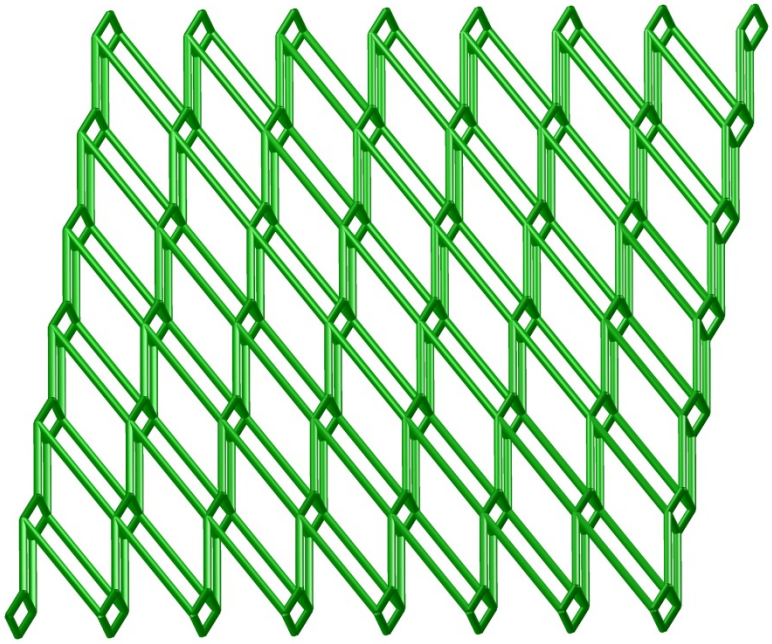

(b)

Fig. 14. The structure of **14**, showing (a) part of an infinite 2D layer, and (b) the 2D topological network.